

THE CAPTURE AND RETENTION OF SULFUR SPECIES BY
CALCIUM COMPOUNDS DURING THE COMBUSTION OF PULVERIZED COAL

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1. INTRODUCTION

Coal is the United States most abundant source of fossil fuel energy however its utilization poses several problems for society, among which are those associated with the formation of atmospheric pollutants during its combustion. Coal is not a pure hydrocarbon fuel, it contains inorganic matter (ash), nitrogen and sulfur which, in turn, form particulates (fly ash), nitrogen oxides and sulfur oxides. The emission of such pollutants to the atmosphere is undesirable and can be avoided by removing the pollutants from the combustion products, preventing their formation, or removing the constituents which form pollutants from the coal. This paper describes bench scale experiments which will establish whether and under which conditions calcium containing sorbents can be used to capture sulfur during pulverized coal combustion. Having established that sulfur capture is possible, the studies will then concentrate upon whether it is practical since sorbent injection into boilers could have a serious impact upon boiler operation. Sorbent injection will increase particulate mass loading, change slagging and fouling characteristics and will change fly ash properties.

The use of sorbents to control emissions of sulfur oxides from coal fired power plants is a conceptually simple process. A pulverized, calcium containing sorbent is injected into the combustion chamber of a boiler where it flash-calcines to lime (CaO) and, at the same time, reacts with sulfur dioxide and oxygen to form calcium sulfite and/or calcium sulfate. Considerable effort was expended in the late 1960's and early 1970's on development and demonstration projects (1), and although pilot plant studies showed promise, the results could not be duplicated in full scale systems. The lack of success was attributed to a combination of loss of reactivity of the lime due to deadburning and maldistribution of the sorbent. Recent pilot scale studies (2, 3) with low NO_x coal burners suggest that sorbent injection could be more effective under conditions which minimize NO_x formation in pulverized coal flames.

Nitrogen oxides are formed from two sources during pulverized coal combustion; molecular nitrogen which is part of the combustion air and nitrogen which is chemically bound in the organic coal matrix. Low NO_x pulverized coal burners are effective because they produce a fuel rich zone which minimizes fuel NO formation and lowers peak flame temperatures, which, in turn, reduces the rate of thermal NO production. If a sorbent is injected into a combustor fired with low NO_x burners it will experience lower peak temperatures and more reducing conditions than if the combustor was fired with "normal" burners. The opportunity to control both nitrogen and sulfur oxide emissions by preventing their formation may be given by the use of sorbent injection into low NO_x burners.

Sulfur capture by sorbent injection involves three processes, namely:

- Sorbent activation - the sorbent particles are heated and calcined. Ultimate particle reactivity will depend mainly upon initial properties and peak particle temperature. If the particle temperatures are too high, the sorbent loses its reactivity (deadburns).
- Capture - sulfur species (H_2S , COS or SO_2) react with the sorbent producing either sulfate or sulfide. The rate of absorption will depend upon

temperature, sulfur species concentration and sorbent characteristics.

- Regeneration - under certain conditions, the spent sorbent may decompose regenerating gas phase sulfur species.

The general reaction describing sulfur capture under oxidizing conditions is:



The rate of this reaction, the rate of calcination, and the maximum calcium utilization imposed by pore blockage has been studied extensively in thin bed and dispersed flow reactors by several workers (4, 5). None of these studies duplicated the time temperature conditions that prevail in pulverized coal flames.

Borgwardt (6) has suggested that reactions such as:



involving reduced sulfur species could become significant under fuel rich conditions. Extrapolation of rate data for such reactions (obtained by Ruth and Squires (7)) to pulverized coal flame conditions indicates that the reaction of H_2S with CaCO_3 is sufficiently fast to allow significant sulfur capture.

Consequently, it appears that there are two possible modes of sulfur capture by calcium based sorbents in a pulverized coal fired combustor operating under low NO_x conditions. Under oxidizing conditions, reduced peak temperatures will reduce deadburning and allow reaction 1 to proceed. If the sorbent is injected into the fuel rich region, reaction 2 may become significant, but calcium sulfide could be lost when the partially oxidized fuel is burned out. Thus retention of the sulfur becomes an important factor in the overall process. Figure 1 shows the effect of temperature and stoichiometric ratio on equilibrium calcium distribution. It indicates that under rich conditions (50% theoretical air) calcium sulfide is very stable compared to calcium sulfate under lean conditions (100% theoretical air or $\text{SR} = 1.0$). These calculations imply that if the sulfide is formed in the rich zone, then the transition to oxidizing conditions should be carried out quickly to prevent prolonged times under new stoichiometric conditions, and that the temperature during this transition should be reduced. An experimental study has been carried out to determine whether either of the two routes referred to above are likely to allow simultaneous control of sulfur and nitrogen oxide emissions from pulverized coal fired boilers.

2. EXPERIMENTAL

A bench scale facility has been constructed which is capable of duplicating the history of the solid particles (coal and sorbent) and the products of combustion in a pulverized coal fired power plant. As shown in Figure 2, the system consists of three major components:

- The radiant furnace, a horizontal refractory lined cyclinder, which simulates the region close to the burners. Heat extraction is varied by adding or removing cooling tubes.
- The post flame cavity which simulates the volume above the burner zone of a boiler before the superheater.
- The convective section, cooled by banks of air cooled stainless steel tubes, which simulates the superheater, reheater and air heater sections of the boiler.

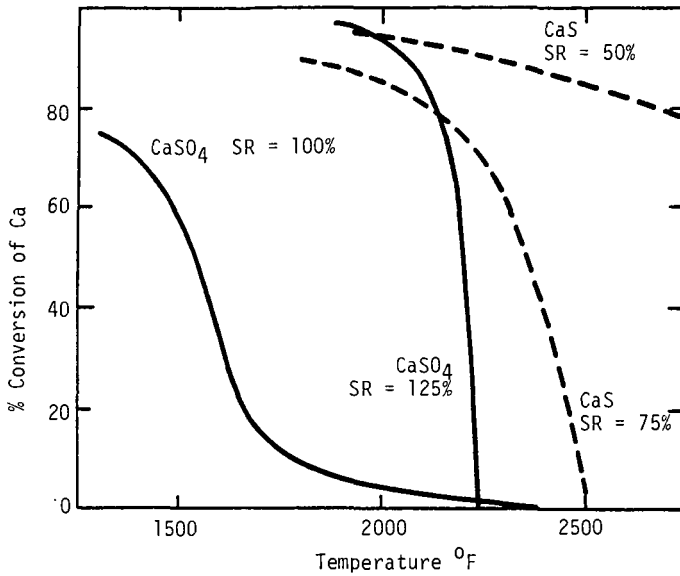


Figure 1. Effect of Temperature and Stoichiometric Ratio on Equilibrium Calcium Distribution - % Ca as CaSO_4 or CaS ($\text{Ca/S} = 1$)

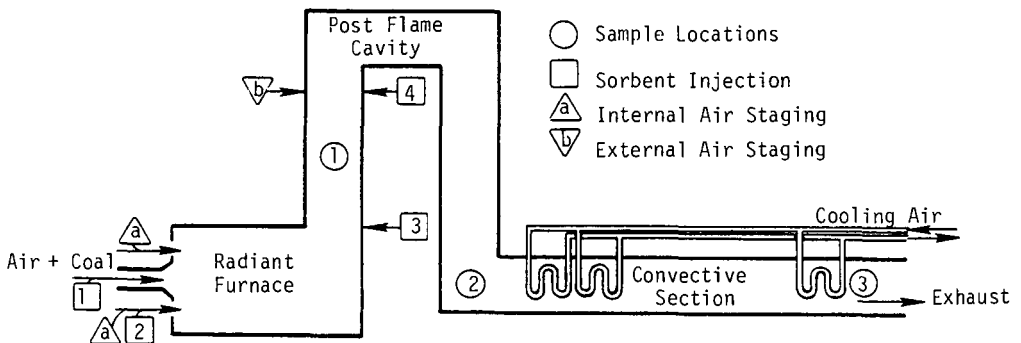


Figure 2. Schematic of Test Furnace Showing Location of Sample Ports, Staged Air Addition and Sorbent Injection.

The facility is fired with coal using a small scale low NO_x burner which could be operated in two modes - internally and externally staged. When the burner was operated with the second stage air supplied at the firing face through the staged air injectors, only the burner zone was fuel rich. This is referred to as internally staged. Alternatively, when the staging air was added downstream in the post flame cavity, the whole of the radiant furnace operated fuel rich. This is referred to in the text as external staging. The sorbent was added in any of four locations: 1) with the coal, 2) with the staged air at the burner face, 3) at the entry of the post flame cavity, and 4) with the downstream staged air when operating in the externally staged mode.

The measurement of sulfur species in combustion products containing active sorbents introduces several problems related to sample acquisition. A "phase discrimination" probe has been designed, constructed and tested which minimizes gas-solid contacting after sample extraction. SO_2 was measured with a non-dispersive ultra-violet absorption instrument. H_2S and COS were measured by gas chromatography using a flame photometric detector. Sulfur capture was based on SO_2 measurements with and without sorbent in every test case.

3. RESULTS

A series of experiments has been carried out with the coal and sorbent listed in Tables 1 and 2 in both the external and internal staging modes.

Indiana Coal	
Ultimate Analysis, % Dry Basis	
C	69.91
N	5.18
H	1.54
S	2.53
O	11.00
Ash	9.84
Calorific Value (dry basis)	12,515 Btu/lb
Moisture, average, as burned	7.0%

Table 1. Coal Properties

Vicron 45-3, Pfizer	
Composition, typical, %	
CaCO_3	97.0
MgCO_3	1.6
SiO_2	1.0
Al_2O_3	0.5
Fe_2O_3	0.05
Moisture	0.2
Specific Gravity	2.71
Particle Shape	rhombic
Oil absorption	14
Surface area (m^2/gm)	1.4

Table 2. Sorbent Properties

Internal Staging

Figure 3 shows the percentage capture as a function of the calcium to sulfur molar ratio when the sorbent was added with the staged air (location 2), and an additional 15% (over the normal heat loss) of the input heat was extracted from the radiant zone. Data are presented showing the relative capture in the radiant zone (sample port 1), the post flame section (between 1 and 2) and the overall capture (sample port 3). The capture in the post flame section is based upon the gas phase sulfur dioxide concentration entering the section and free calcium oxide (that which was not used in the radiant section). The data presented in Figure 3 indicate that when heat is extracted from the radiant zone capture occurs in both the radiant zone and the post flame section. These data were obtained with the burner zone operating at a stoichiometric ratio of 0.6 and a total air input equal to 120% of stoichiometric.

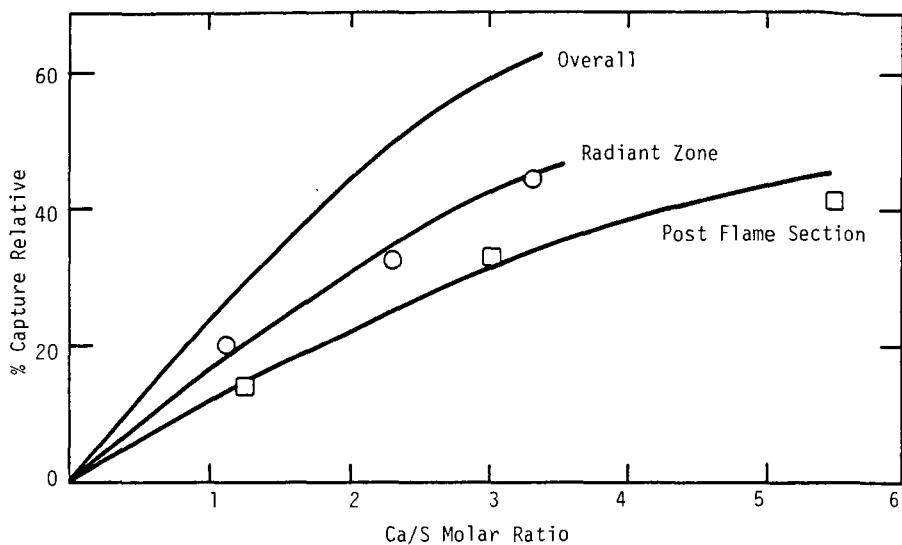


Figure 3. Relative SO_2 Capture, Sorbent Injected With the Staged Air Internal Mode With Heat Extraction in the Radiant Zone.

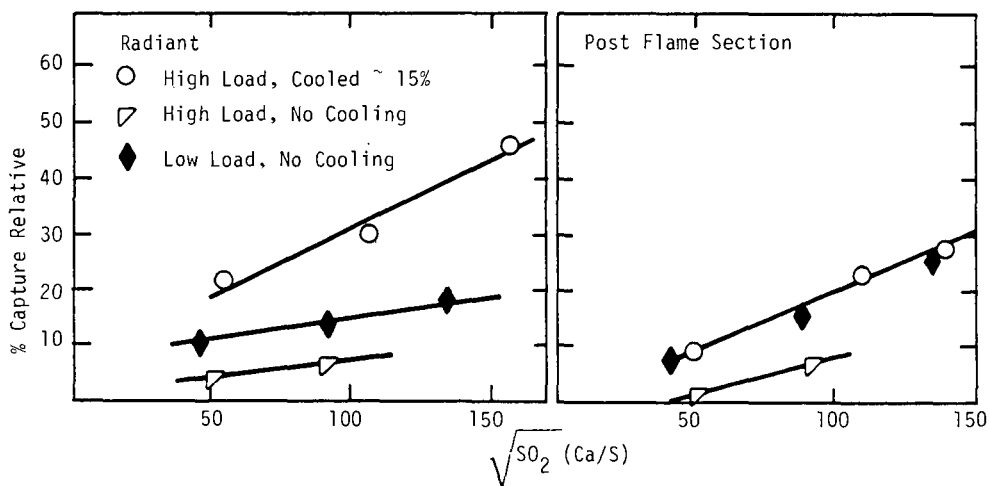


Figure 4. The Impact of Load and Radiant Zone Cooling on Sulfur Capture.

Tests have been carried out to determine the influence of burner zone stoichiometry on sulfur capture in the internally staged mode. Provided the burner zone stoichiometry does not rise above 80% the sulfur capture appears almost to be independent of burner zone stoichiometry. However as the staging air is reduced to a minimum and the burner zone becomes fuel lean the sulfur capture is reduced. In these experiments this reduction is probably caused by a reduction in sorbent velocity and because of the increase in peak flame temperatures as the burner zone stoichiometry increases.

In the internal staging mode thermal environment has a very significant impact upon sulfur capture. This is illustrated by the data presented in Figure 4 which shows the sulfur capture in both the first two zones as a function of the product of the calcium to sulfur ratio and the square root of the sulfur dioxide concentration in that zone. Three conditions are shown: high load with and without radiant zone cooling and low load without cooling. Reducing the load will lower temperatures and increase residence times. At high load cooling the radiant zone dramatically increases the sorbent reactivity. At low load reactivity in the radiant zone is less than that with cooling at high load but the reactivity in the post flame section is similar to the high load, cooled case.

External Staging

The purpose of the external staging tests was to determine whether sulfur dioxide emissions could be reduced by adding limestone under reducing conditions and then burning the fuel completely by the addition of second stage air downstream. This requires that the majority of the sulfur captured under reducing conditions be retained by the sorbent as the fuel burns out. Equilibrium calculations indicate that under fuel rich conditions hydrogen sulfide is the dominant sulfur species while measurements in the fuel rich region indicate that sulfur dioxide, hydrogen sulfide and carbonyl sulfide all are present. Sulfur dioxide concentrations decrease and hydrogen sulfide concentrations increase as the primary zone stoichiometry decreases. Thus, the sorbent may react with any of three sulfur species. Initial reaction rates for the reaction of H_2S and COS with CaO have been measured (7, 8) and are similar.

The data from two different external staging experiments are shown in Figures 5 and 6. In one experiment sorbent was added with the coal (location 1) and measurements of sulfur species at the exit of the rich zone (port 2) were made with and without sorbent. Figure 5 shows the percent capture of SO_2 , COS and H_2S as a function of first stage stoichiometric ratio. It can be seen that all three species were captured. The data in Figure 6 are from an experiment comparing calcium utilization firing with two fuels, coal and propane doped with H_2S to give the same sulfur content as the coal. The sorbent was added at the base of the post flame section (location 2) and the staging air was added in the post flame cavity (location b). SO_2 was measured with and without sorbent for both fuels at sample port 3 (exit of furnace). Total calcium utilization as a function of first stage stoichiometry is shown in Figure 6. Measurements indicate that as much as 50 percent of the input coal remains as solid at the lower first zone stoichiometries. The data for coal presented in Figure 6 has been plotted as a function of the actual gas phase stoichiometry. It can be seen that the ultimate sulfur capture decreased with decreasing gas phase stoichiometric ratio for coal but increased for propane doped with H_2S . It should be noted that the data shown in Figure 6 represent the sum of sulfur species capture under reducing conditions in the first zone, retention of sulfur during burnout and the sulfur capture under oxidizing conditions in the second stage.

4. CONCLUSIONS

An investigation has been carried out in a bench scale facility to determine

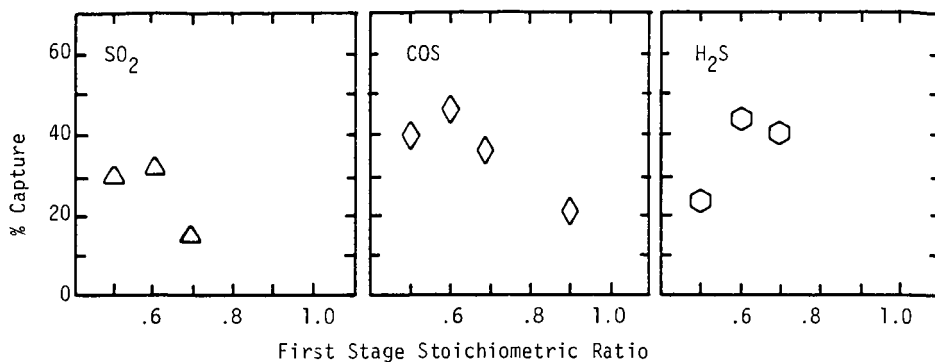


Figure 5. % Capture of Sulfur Species in Rich First Stage (External Mode) Sorbent Injected With the Coal.

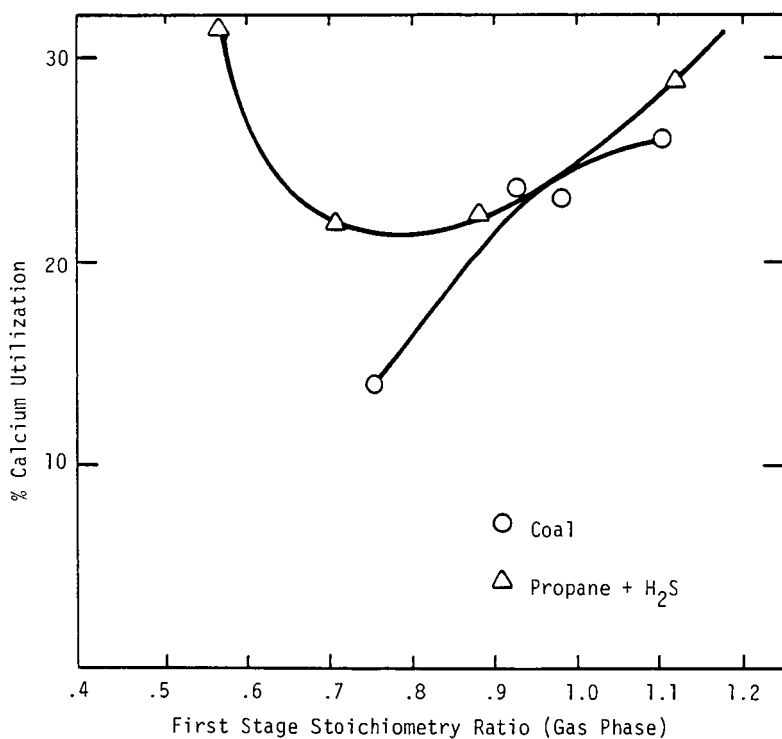


Figure 6. Capture and Retention of Sulfur Under External Staged Conditions for Coal and Propane Doped with H₂S.

under which conditions sulfur species generated during the combustion of pulverized coal can be captured and retained by calcium containing sorbents. Two series of experiments were carried out: one in which any capture would take place primarily under oxidizing conditions and the other in which significant residence times in the rich zone would allow capture under reducing conditions. Under oxidizing conditions the thermal environment experienced by the sorbent particle appears to be the dominant parameter controlling sulfur capture. This is probably because of dead-burning. If a sorbent particle's temperature exceeds a certain limit (which depends on the particular sorbent) the sorbent deadburns and loses its reactivity (4).

The processes controlling capture and retention when the sorbent is maintained under reducing conditions for a prolonged time are more complex. The principle gas phase sulfur species are H_2S , SO_2 and CO_2S and, even though the sulfur species are absorbed the possibility that the sulfide will decompose during burnout exists. The data presented in Figure 6 shows a significant difference between the behavior of coal and propane doped with H_2S . This difference can be attributed to:

- With coal part of the fuel remains in the solid phase and for a given input stoichiometry the gas phase stoichiometry in the reducing zone is higher than with gas. Reference to Figure 1 indicates that the stability of calcium sulfide is strongly dependent upon stoichiometry ratio;
- With coal up to 50 percent of the sulfur remains in the solid phase under rich conditions thus the gas phase concentration is lower than the corresponding concentration with propane as the fuel;
- The conditions during burnout in the second stage will be different for the solid and gaseous fuels and this could affect retention of the sulfur during burnout.

These tests indicate that there is the potential to remove greater than 50 percent of the input sulfur with Ca/S molar ratios of two when coal is burned under low NO_x conditions. Further work is necessary to insure that the controlling conditions can be achieved in practical combustors and that the sorbent injection does not adversely impact combustor performance.

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